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(54) A PROCESS FOR PREPARING ISOCYANATE AND ISOCYANATE-BASED DERIVATIVES OF CERTAIN AMINO-1,3,5-TRIAZINES BY DIRECT PHOSGENATION

VERFAHREN ZUR HERSTELLUNG VON ISOCYANATEN UND VON ISOCYANATABGELEITETEN DERIVATEN VON BESTIMMTEN AMINO-1,3,5-TRIAZENINEN DURCH DIREKTE PHOSGENIERUNG

PROCEDE DE PREPARATION DE DERIVES ISOCYANATES OU A BASE D'ISOCYANATES A PARTIR DE CERTAINES AMINO-1,3,5-TRIAZINES, PAR TRAITEMENT DIRECT AU PHOSGENE

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EP-A- 0 566 774
US-A- 3 919 221
US-A- 4 939 213

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates to the preparation of isocyanate and/or isocyanate-based 1,3,5-triazine derivatives by the direct phosgenation of certain amino-1,3,5-triazines having at least three unsubstituted amino groups attached to the triazine ring(s).

Description of Related Art

[0002] Various derivatives of amino-1,3,5-triazines are described in the literature as being utilized in a wide variety of fields. An important use of certain of these derivatives, such as alkoxymethyl derivatives of melamine and guanamines, is as crosslinkers and/or reactive modifiers in curable compositions which contain resins having active hydrogen groups. While alkoxymethylated melamines and guanamines provide excellent results in a number of aspects, they also have the disadvantage of releasing formaldehyde as a volatile by-product under curing conditions. It has long been a desire of industry to find acceptable alternatives which do not emit formaldehyde upon cure.

[0003] One such alternative which has shown great promise is carbamate functional 1,3,5-triazines disclosed in the commonly owned U.S. Patent No. 4,939,213, U.S. Patent No. 5,084,541, U.S. Patent No. 5,288,865, EP-A-0604922, EP-A-0624577 and United States Application Serial No. 08/138,581 (filed. October 15, 1993).

[0004] The carbamate functional 1,3,5-triazines disclosed in these references are believed to act in a manner similar to blocked isocyanates, and have been found to be particularly useful as crosslinkers in coating compositions based upon hydroxy functional resins, with the cured coatings possessing a wide range of desirable properties.

[0005] One impediment to the commercial use of these carbamate functional 1,3,5-triazines has been that known processes for their preparation have been somewhat cumbersome, difficult and expensive. For example, in U.S. Patent No. 4,939,213 and U.S. Patent No. 5,084,541, 1,3,5-triazine carbamates are produced in a two step process by first reacting an amino-1,3,5-triazine with oxalyl chloride to produce an isocyanate which is then converted to the corresponding carbamate by reaction with an alcohol. Further, in U.S. Patent No. 5,288,865, carbamate functional 1,3,5-triazines are produced in a one-step process by reacting a haloamino-1,3,5-triazine with an acid halide. The primary disadvantages with these processes include the use of somewhat exotic and/or expensive halogenated starting materials and low ultimate yield of the desired products.

[0006] Many of these disadvantages have been overcome by the process disclosed in EP-A-0624577, wherein carbamate functional 1,3,5-triazines are produced by reacting an at least bis-amino 1,3,5-triazine with an acyclic organic carbonate in the presence of a strong base.

[0007] Another process which overcomes many of these disadvantages is disclosed in United States Application Serial No. 08/138,581, wherein isocyanate functional 1,3,5-triazines are produced by the carbonylation of (halo)amino 1,3,5-triazines with carbon monoxide, in the presence of a metal promoter for promoting carbonylation.

[0008] An alternative process is disclosed by US-A-3919221 comprising reacting s-triazinyl-mono- or -diamines with phosgene in certain organic solvents, such as nitrobenzene.

[0009] It has now been surprisingly discovered that isocyanate functional 1,3,5-triazine derivatives can also be prepared from amino-1,3,5-triazines having at least three unsubstituted amino groups attached to the triazine ring, such as melamine, by direct phosgenation. These isocyanate functional 1,3,5-triazines may be further derivatized by contacting the same with a wide variety of well-known isocyanate-reactive materials. For example, these isocyanates may be readily "blocked" (for example, converted to the corresponding carbamate) by adding a blocking agent (such as a hydroxyl compound) to the isocyanate functional 1,3,5-triazine without isolating it. In addition, these isocyanates may be readily oligomerized by adding a multifunctional isocyanate-reactive compound (for example, a diol or diamine) to the isocyanate functional 1,3,5-triazine without isolating it.

[0010] It should be noted that it is generically known to obtain isocyanates by direct phosgenation of amines. It is, however, also well known that the amine functionality of amino-1,3,5-triazines, such as melamine, is not equivalent to other types of typical amine functionality. Significantly, melamines are among the least reactive of the "amines" and the most difficult to functionalize, and their behavior cannot normally be correlated to that of other known amines.

[0011] For example, most "typical" amines are highly reactive with acid halides. In a publication by E.M. Smolin and L. Rappaport entitled "S-Triazines and Derivatives," Interscience Publishers Inc., New York, page 333 (1959), it is reported that attempts to react an acid halide with the amino group on a 1,3,5-triazine such as melamine were not successful. Further, attempts to functionalize amino-1,3,5-triazines often results in substitution at the nitrogen on the triazine ring. For example, it is known that the reaction of melamine with alkyl halides, such as allyl chloride, results in alkyl substitution at the nitrogen on the triazine ring resulting in isomelamine derivatives.

[0012] Indeed, it is reported in U.S. Patent No. 3,732,223 that the well-known phosgenation of amines fails to produce isocyanate functionality when applied to amino-1,3,5-triazines. In subsequent U.S. Patent No. 3,919,221, the phosgenation of amino-1,3,5-triazines having one or two unsubstituted amino groups attached to the triazine ring to obtain monoisocyanate and diisocyanate triazines is reported to occur under certain specified conditions. Both of the above patents are incorporated by reference herein as if fully set forth.

[0013] It appears, however, that procedure generically described in previously incorporated U.S. Patent No. 3,919,221 does not effectively or significantly proceed with amino-1,3,5-triazines having at least three unsubstituted amino groups attached to the triazine ring(s), such as melamine (2,4,6-triamino-1,3,5-triazine). Without wishing to be bound by any particularly theory, it is believed that solubility constraints of these (at least tris-unsubstituted amino)-1,3,5-triazines, in conjunction with the difficulties associated with the functionalization of amino-1,3,5-triazines in general, may hinder the reaction of such compounds with phosgene under the reaction conditions reported in the reference.

[0014] Surprisingly, a procedure has now been discovered in which phosgene (and phosgene sources) can readily and effectively be directly reacted with such (at least tris-unsubstituted amino)-1,3,5-triazines (direct phosgenation) to produce the corresponding isocyanate functional 1,3,5-triazine derivatives, which can further be readily and effectively reacted with known isocyanate-reactive materials (such as blocking agents) to produce the corresponding isocyanate-based derivatives thereof.

SUMMARY OF THE INVENTION

[0015] In accordance with the present invention, there is provided a process for preparing isocyanate functional derivatives by contacting (i) an amino-1,3,5-triazine and (ii) phosgene in a reaction system, at a temperature of 51.4°C to 120°C a pressure of 50 psig (3.45×10^5 Pa) to 1000 psig (6.9×10^6Pa) and for a length of time sufficient to produce an isocyanate functional 1,3,5-triazine derivative and hydrogen chloride, whereby the amino-1,3,5-triazine is an (at least tris-unsubstituted amino)-1,3,5-triazine, the reaction is conducted under conditions whereby the hydrogen chloride is gaseous and the phosgene is refluxed and at least a portion of the hydrogen chloride is removed from the reaction system as such hydrogen chloride is generated during the reaction of (i) and (ii) by passing an inert gas through the pressurized and heated reaction system during the reaction.

[0016] Isocyanate-based derivatives of the (at least tris-unsubstituted amino)-1,3,5-triazines can readily be produced by reacting an isocyanate-reactive material with the isocyanate functional 1,3,5-triazine product formed by the reaction of (i) and (ii).

[0017] An important step of the process of the present invention requires that the by-product hydrogen chloride be at least partially removed as it is generated by the reaction of phosgene with the (at least tris-unsubstituted amino)-1,3,5-triazine. This is achieved by conducting the reaction under pressure and temperature conditions whereby the phosgene is refluxed and the by-product hydrogen chloride is gaseous.

[0018] As indicated above, an isocyanate functional 1,3,5-triazine product is produced by contacting (i) and (ii), which may be reacted with isocyanate-reactive materials to produce various isocyanate-based derivatives. For example, the isocyanate groups may be blocked by contacting the isocyanate functional 1,3,5-triazines with known isocyanate blocking agents, such as certain active-hydrogen containing compounds. As another example, oligomers of the isocyanate functional 1,3,5-triazines can be produced by contacting the same with multifunctional isocyanate reactive materials such as diols and diamines. The phrase "isocyanate and/or isocyanate-based" 1,3,5-triazines, in the context of the present invention, includes triazine derivatives having isocyanate functionality, isocyanate-based functionality, or a mixture of isocyanate and isocyanate-based functionality. For example, when a blocking agent is added in an amount which is less than the molar equivalent of the available isocyanate functionality, then a triazine derivative is produced having both isocyanate and blocked-isocyanate functionality.

[0019] The process of this invention is advantageous because no exotic and costly starting materials, and particularly no halogenated amino-1,3,5-triazine starting materials, are required. Further, (at least tris-unsubstituted amino)-1,3,5-triazines can, for the first time, be directly phosgenated via generally conventional procedures largely known and currently utilized on large industrial scales, which procedures can readily be modified as required by the present inventive process. Moreover, the (at least tris-unsubstituted amino)-1,3,5 triazines, such as melamine, can be directly reacted with phosgene, followed by reaction of the isocyanate with any one of a wide variety of well-known isocyanate reactive materials to obtain an isocyanate-based 1,3,5-triazine without handling or isolation of the isocyanate triazine product.

[0020] A preferred use for the isocyanate functional 1,3,5-triazines and various derivatives thereof is as a crosslinking agent with polyfunctional active hydrogen containing resins such as hydroxy functional acrylic or polyester resins, for producing curable compositions which have utility in coatings, adhesives, molding and other applications. This and other uses are disclosed in various of the previously incorporated references.

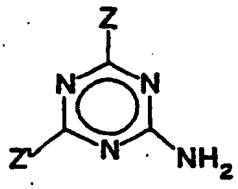
[0021] These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] As indicated above, the present invention is a novel process for preparing isocyanate functional 1,3,5-triazines by contacting an (at least tris-unsubstituted amino)-1,3,5-triazine with phosgene. The process is carried out at a temperature of 51.4°C to 120°C, pressure of 50 psig (3.45×10^5 Pa) to 1000 psig (6.9×10^6Pa) and for a sufficient time, and further under conditions which allow removal of at least a portion, and preferably a substantial portion, of the reaction-generated hydrogen chloride from the reaction system as it is generated, resulting in the formation of the corresponding isocyanate functional 1,3,5-triazines. In general, each unsubstituted amino group on the amino-1,3,5-triazine will be converted to an isocyanate group; consequently, the direct phosgenation of a (tris-unsubstituted amino)-1,3,5-triazine, such as melamine, in accordance with the present invention will result in the corresponding tris-isocyanate product.

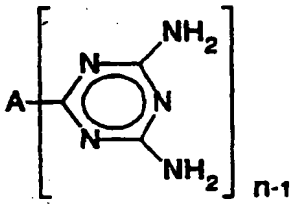
[0023] When an isocyanate-reactive material such as a well-known isocyanate blocking agent is added subsequent to the formation of the isocyanate functional 1,3,5-triazine, there is obtained the corresponding 1,3,5-triazine with isocyanate-based (blocked isocyanate) functionality. More highly functional derivatives of such isocyanate functional 1,3,5-triazines can also be produced by adding subsequent to the formation of the isocyanate functional 1,3,5-triazine a multifunctional isocyanate reactive material. The (At Least Tris-Unsubstituted Amino)-1,3,5-Triazine Starting Materials

[0024] The (at least tris-unsubstituted amino)-1,3,5-triazine starting materials, such as melamine (2,4,6-triamino-1,3,5-triazine) and oligomers thereof, are well known and readily available. The term "at least tris-unsubstituted amino" in the context of the invention is meant to include a monomeric 1,3,5-triazine having three $-NH_2$ groups attached to the triazine ring (melamine), as well as oligomers of various 1,3,5-triazines (e.g., dimers, trimers and tetramers) having a total of at least three $-NH_2$ groups attached to the triazine rings per molecule. The preferred (at least tris-unsubstituted amino)-1,3,5-triazine starting materials are generally represented by the formula:



wherein

Z and Z^1 are independently selected from the group consisting of $-NH_2$, and a group represented by the formula:



wherein

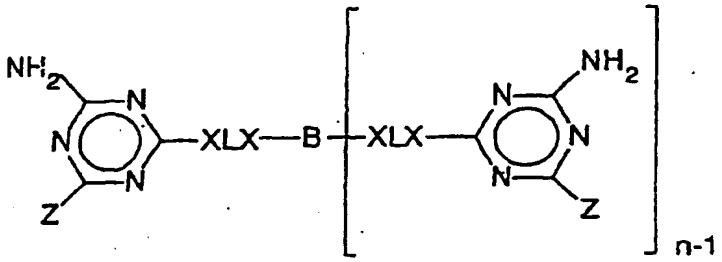
A is an n functional anchor and n is at least 2.

[0025] Preferred for use with the process of the present invention is substantially monomeric melamine, wherein where both Z and Z^1 are $-NH_2$.

[0026] Also suitable are oligomeric versions of melamine which, as is well-known to those of ordinary skill in the art, may be derived from the self-condensation of melamine or the reaction of melamine with a polyfunctional co-reactant. This oligomeric version is represented when one or both of Z and Z^1 are the formula represented above, wherein the group A in the above formula is an n functional anchor which can, for example, be a hydrocarbyl compound residue, an amino compound residue, oxygen or sulfur. "Hydrocarbyl compound residue" in the context of the present invention

refers to the residue of compound based on carbon and hydrogen atoms after abstraction of reacted functionality, as well as substituted derivatives thereof.

[0027] More preferably, the oligomeric (at least tris-unsubstituted amino)-1,3,5-triazines including the group A have the following general formula:



wherein

B is selected from the group consisting of hydrocarbyl compound residue and a hydrocarbyloxy hydrocarbyl compound residue;
each X is independently selected from the group consisting of NH, N(hydrocarbyl), N(hydrocarbyloxy hydrocarbyl), CH_2O, S, CO_2 and $NHCO_2$;
each L is independently selected from the group consisting of a hydrocarbylene and a hydrocarbyleneoxy hydrocarbyl;
n is at least 2; and
Z is as defined above.

[0028] The term "hydrocarbyl" in the context of the present invention, is a group which contains carbon and hydrogen atoms and includes, for example, alkyl, aryl, aralkyl, alkenyl, and substituted derivatives thereof. Likewise, the term "hydrocarbylene" refers to a divalent hydrocarbyl such as, for example, alkylene, arylene, aralkylene, alkenylene, and substituted derivatives thereof.

Phosgene

[0029] Phosgene is well-known to those of ordinary skill in the art as being represented by the formula ClC(O)Cl. Phosgene, as defined within the context of this invention, also includes phosgene analogs capable as serving as a phosgene source,

[0030] Exemplary phosgene analogs include, without limitation, diphosgene and triphosgene. Diphosgene (trichloromethyl chloroformate) and triphosgene (trichloromethyl carbonate) are represented, respectfully, by the formulas $ClC(O)CCl_3$ and $Cl_3COC(O)OCCl_3$. Triphosgene is known by those skilled in the art to be a phosgene source. See, e.g., M. J. Coghlan and B. A. Caley, "Trichloromethyl Carbonate as a Practical Phosgene Source" Tetrahedron Letters, Vol. 30, No. 16, pp. 2033-2036 (1989). the present invention.

The Isocyanate-Reactive Materials

[0031] As mentioned earlier, isocyanate-based 1,3,5-triazine derivatives can readily be produced in accordance with the present invention by post-reacting the isocyanate functional 1,3,5-triazine with an isocyanate-reactive material such as an active-hydrogen containing compound.

[0032] A wide variety of active-hydrogen containing compounds are suitable for use in forming isocyanate-based derivatives, such as carbamates, and are described in detail in the previously incorporated references. For instance, the active-hydrogen containing compounds employed in this process include those known to one skilled in the art which have at least one active-hydrogen moiety selected from the group consisting of carboxyl, hydroxyl, thiol, sulfonamide, amido, primary amine, secondary amine, salts thereof and mixtures thereof. As preferred examples may be mentioned alcohols, phenols, oximes, hydroxamic ethers, lactams and mixtures thereof.

[0033] As a specific preferred example, carbamate functional 1,3,5-triazine derivatives can be formed by reacting the isocyanate functional triazines with hydroxyl group-containing compounds. As suitable hydroxyl group-containing

compounds may be mentioned, for example, straight or branched monohydric or polyhydric alkanols and alkenols having 1 to 20 carbon atoms per molecule, monohydric or polyhydric cycloalkanols and cycloalkenols having 3 to 20 carbon atoms in the molecule, and monohydric and polyhydric arylalkyls having 7 to 20 carbon atoms per molecule. Further, these alcohols may also have a substituent such as a halogen atom, a cyano group, an alkoxy group, a sulfoxide group, a sulfone group, a carbonyl group, an ester group, an ether group and an amide group. Mixtures of the above are also suitable.

[0034] Preferred of the above are the aliphatic linear, cyclic, saturated, or unsaturated alcohols having 1 to 8 carbon atoms, as well as mixtures thereof. As specific preferred examples may be mentioned methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, iso-butanol, tert-butanol, pentanol, hexanol, cyclohexanol, heptanol, octanol, ethylhexyl alcohol, benzyl alcohol, allyl alcohol, ethylene chlorohydrin, ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, ethoxyethanol, hydroxyethoxyethanol, 1-methoxy-2-propanol and mixtures thereof.

[0035] Phenols are also suitable as the hydroxyl group-containing compound. As specific examples may be mentioned phenol, various alkyl phenols, various alkoxy phenols, various halogenated phenols, dihydroxybenzene, 4,4-dihydroxydiphenylmethane, various bisphenols such as bisphenol-A, and hydroxynaphthalenes. As specific preferred examples may be mentioned phenol, 2-methyl phenol, 3-methyl phenol, 4-methyl phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, catechol, resorcinol, hydroquinone, and mixtures thereof.

[0036] Many of the aforementioned hydroxyl group-containing compounds are well-known isocyanate blocking agents. Other well-known isocyanate blocking agents are also suitable for use herein, and include, for example, those blocking groups which deblock at relatively low temperatures, e.g., below about 125°C, such as an oxime of an aldehyde or ketone (e.g., methylethyl-ketoxime, acetone oxime and cyclohexanone oxime), lactam (e.g., caprolactam), hydroxamic acid ester, imidazole, pyrazole, N-hydroxyimide (e.g., N-hydroxyphthalimide), dimethylamine, or other blocking groups such as recited in U.S. Pat. No. 4,444,954 the pertinent portions of which are incorporated by reference herein as if fully set forth.

[0037] For use as a crosslinking agent as described in various of the previously incorporated reference, most preferred for the isocyanate-reactive compound are aliphatic alcohols and ether-alcohols having 1 to 18 carbons, such as methanol, ethanol, isopropanol, propanol, isobutanol, n-butanol, t-butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, lauryl alcohol, 2-ethyl hexanol, alkyl alcohol, glycidol, stearyl alcohol, ethoxyethanol and 1-methoxy-2-propanol.

Process Conditions

[0038] In the process of the present invention, the (at least tris-unsubstituted amino)-1,3,5-triazine and phosgene (or phosgene source or equivalent) are contacted in a reaction system at a temperature of 51.4°C to 120°C pressure of 50 psig (3.45×10^5Pa) to 1000 psig (6.9×10^6Pa), and length of time sufficient to produce the desired isocyanate-functional 1,3,5-triazine. Significantly, at least a portion (and preferably a substantial portion) of the hydrogen chloride generated from the reaction of the components is removed from the reaction system as it is generated during the reaction. The hydrogen chloride by-product can be removed from the reaction system by venting or by the use of a hydrogen chloride scavenger (preferably which does not release water) such as, for example, calcium oxide or other Group II oxides. The components are contacted under conditions whereby the hydrogen chloride is gaseous while the phosgene is refluxed, with the removal of the hydrogen chloride being facilitated by passing an inert gas, such as argon or nitrogen, through the pressurized and heated reaction system during the reaction.

[0039] The relative amounts of the (at least tris-unsubstituted amino)-1,3,5-triazine and phosgene employed in the process is generally in the range of about 1:3 to about 1:250, and most preferably in the range of about 1:10 to about 1:30, on a weight basis.

[0040] The reaction system of the present invention is not limiting, and can be any reaction system, such as a vessel or container, which can be subject to the conditions required to obtain the desired isocyanate functional 1,3,5-triazine. The reaction system includes as means for removing the hydrogen chloride by-product during the reaction of the components venting with inert gases . An exemplary system is set forth in Example 1 described herein.

[0041] The reaction components are preferably contacted under temperature and pressure conditions at which the by-product hydrogen chloride is gaseous and the phosgene is refluxed during the reaction. The reaction temperature ranges from above the critical temperature of hydrogen chloride (51.4°C) up to 120°C. In addition, the reaction of the components is conducted at a pressure in the range from 50 psig (3.45×10^5 Pa) to 1000 psig (6.9×10^6 Pa), and preferably from about 100 psig (6.9×10^5 Pa) to about 200 psig (1.38×10^6 Pa), depending upon the reaction temperature. At these temperatures and pressures, the reaction has been found to produce isocyanate functional 1,3,5-triazine in a period of time ranging from about 6 hours to about 72 hours.

[0042] It is preferred to conduct the reaction in the presence of a liquid medium which is not readily reactive with phosgene (and preferably inert under reaction conditions) such as, for example, nitrobenzene, chlorobenzene, dichlorobenzene, various ethers and polyethers, as well as mixtures thereof. The reaction may be aided by the inclusion of

a catalyst in the reaction mixture such as, for example, molecular halides and phosphorous halides.

[0043] As previously indicated, to obtain significant conversions at least a portion of the generated hydrogen chloride is removed from the reaction system as it is generated during the reaction. Most preferably, the removal of the reaction-generated hydrogen chloride is achieved by pressurizing the reaction system with an inert gas and heating the reaction components to a temperature which results in the selective distillation of mostly hydrogen chloride and not phosgene. The distilled hydrogen chloride is removed from the reaction system by venting the system with an inert gas, such as argon or nitrogen. The temperature of the reaction components and the pressure of the reaction systems may be readily adjusted by those skilled in the art to maximize the removal of hydrogen chloride and minimize the loss of phosgene during the reaction.

[0044] The isocyanate functional 1,3,5-triazine prepared by the above-described process may subsequently be reacted with the isocyanate-reactive material as described in various of the previously incorporated references. Generally, the isocyanate functional 1,3,5-triazine and isocyanate-reactive material may be reacted at temperatures ranging from about -20°C to about 200°C, and for varying times, depending on the isocyanate-reactive material. For most suitable blocking agents, the components are reacted at a temperature ranging from about 20°C to about 40°C when adding the blocking agents. Such blocking reaction is carried out to substantial completion, generally for a time ranging from about 10 minutes to about 2 hours. The resulting isocyanate-based 1,3,5-triazines can be isolated in any desired manner, such as by filtration and distillation of the solvent.

[0045] The relative amount of isocyanate blocking agent material added to the isocyanate functional 1,3,5-triazine is generally in the range of about 3:1 to about 30:1 equivalents of isocyanate reactive functionality per isocyanate group. Preferably, the ratio is in the range of about 3:1 to about 5:1 on such equivalent basis.

[0046] If the active-hydrogen containing compound added to the reaction is less than the molar equivalent of available isocyanate functionality, then the resulting 1,3,5-triazine will have a mixture of isocyanate and isocyanate-based functionality. When utilized as a "blocked isocyanate" crosslinking agent, it is preferred to add an amount of blocking agent which will react to form a fully blocked-isocyanate functional 1,3,5-triazine.

[0047] The examples which follow are intended as an illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied.

EXAMPLE 1

Preparation of Tris-n-Butylcarbamoyl-1,3,5-Triazine by Direct Phosgenation of Melamine and the Addition of N-Butanol

[0048] One end of a 22 mm diameter, 285 mm long, heavy wall quartz tube was fitted with a Hastelloy C-276 end cap. The other end of the tube was flame sealed closed into a rounded bottom. A 35 mm diameter, 90 mm long water condenser was positioned concentrically onto the outside of the quartz tube approximately 40 mm from the closed end. This condenser was constructed as follows. Rubber stoppers were placed into either end of a 35 mm diameter, 90 mm long section of glass tubing. This section of glass tubing had water inlet/outlet connections near each end. Each of the rubber stoppers had been bored through the center with a single 22 mm diameter hole which the quartz tube was pushed through so that the rubber stoppers formed a seal between the outside of the quartz tube and the inside of the condenser jacket. The Hastelloy end cap had two 1/8 NPT threaded connections. A pressure regulated, dry argon source was attached to the inlet connection through a stainless steel metering valve. The outlet connection was attached to an electronic, recording pressure transducer and a second stainless steel metering valve by means of a tee. The quartz tube was charged with melamine (97 mg) and nitrobenzene (2 ml). A small Teflon coated, magnetic stirring bar was placed inside the quartz tube and the tube clamped vertically in a fume hood so that the Hastelloy end cap was at the top of the quartz tube reactor. The argon inlet valve was closed and the reaction set up attached to a vacuum manifold through the outlet valve. The reaction mixture of melamine and nitrobenzene was frozen by immersing the end of the reaction tube in a slurry of dry ice and acetone. A cylinder of phosgene was attached to the vacuum manifold. The quartz reaction tube and all connecting lines including those between the phosgene cylinder and vacuum manifold were evacuated. The valve on the vacuum manifold leading to the vacuum pump was closed and the phosgene cylinder valve opened slowly. Approximately 2 ml of phosgene was condensed into the reactor. The phosgene cylinder valve and reactor outlet valve were closed. The dry ice acetone slurry was removed from around the end of the reaction tube and the reaction mixture allowed to warm to room temperature. The vacuum manifold and connecting lines were flushed with dry nitrogen into a caustic scrubber. The reactor was disconnected from the vacuum manifold. The outlet valve from the reactor was attached to a caustic scrubber. The argon inlet valve on the reactor was opened and the pressure adjusted to 175 psig (1.3×10^6 Pa). The outlet valve on the reactor was opened slightly so that a flow of 20 to 30 ml per minute of argon flowed through the reactor above the condenser into the caustic scrubber. The water flow through the condenser was started. The reaction mixture was heated to reflux by placing the lower end of the reactor in a 100°C oil bath. The reaction mixture was stirred with a magnetic stirrer placed under the oil bath. Stirring and refluxing were continued for 62 hours. The water flow through the condenser was stopped. The reactor outlet valve

was opened and the argon inlet valve used to control the flow of argon so that the excess phosgene was vented into the caustic scrubber. The reaction mixture was stirred and heated with the 100°C oil bath for 15 minutes after the reaction mixture quit bubbling from the boiling off of the volatile components of the reaction mixture. The oil bath was lowered and the reaction mixture allowed to cool to room temperature. The Hastelloy cap was temporarily removed and n-butanol (2 ml) added with stirring. The oil bath was raised and the reaction mixture heated with stirring for an additional 15 minutes after the n-butanol addition. The reaction mixture was cooled and filtered. The excess solvent and n-butanol were stripped from the filtrate at room temperature under high vacuum.

[0049] The remaining light tan, solid residue (41 mg) was analyzed by HPLC and found to be mostly trisbutylcarbamoyltriazine.

COMPARATIVE EXAMPLE 1

[0050] The reactor described in EXAMPLE 1 was charged with melamine (96 mg) and nitrobenzene (2 ml). The outlet valve of the charged reactor was attached to a vacuum manifold. The slurry was frozen in dry ice acetone and the reactor evacuated. A cylinder of hydrogen chloride was attached to the reactor inlet valve and the headspace of the reactor filled with hydrogen chloride. The reaction mixture was allowed to warm to room temperature and the hydrogen chloride pressure adjusted to 5 psig (3.4×10^4 Pa). The reactor inlet and the outlet valves were closed. The hydrogen chloride cylinder was disconnected from the inlet valve and replaced with a pressure regulated source of argon. The reaction mixture was frozen with liquid nitrogen. A cylinder of phosgene was attached to the vacuum manifold. The vacuum manifold and all connecting lines were evacuated. The valve leading to the vacuum pump was closed. The phosgene cylinder valve was opened and the reactor outlet valve (now serving as an inlet) was cautiously opened until approximately 2 ml of phosgene had condensed into the reactor. The phosgene cylinder valve and the reactor outlet valve were closed. The vacuum manifold and all connecting lines were flushed with dry nitrogen into a caustic scrubber. The reactor was disconnected from the vacuum manifold. The liquid nitrogen bath was removed from the reactor and the contents of the reactor allowed to warm to room temperature. The argon inlet valve on the reactor was opened and the pressure adjusted to 175 psig (1.3×10^6 Pa). The outlet valve on the reactor remained closed. The water flow through the condenser was started. The reaction mixture was heated to reflux by placing the lower end of the reactor in a 100°C oil bath. The reaction mixture was stirred with a magnetic stirrer placed under the oil bath. Stirring and refluxing were continued for 66.5 hours. The water flow through the condenser was stopped. The reactor outlet was attached to a caustic scrubber. The reactor outlet valve was opened and the argon inlet valve used to control the flow of argon so that the excess phosgene was vented into the caustic scrubber. The reaction mixture was stirred and heated with the 100°C oil bath for 15 minutes after the reaction mixture quit bubbling from the boiling off of the volatile components of the reaction mixture. The oil bath was lowered and the reaction mixture allowed to cool to room temperature. The Hastelloy cap was temporarily removed and n-butanol (2 ml) added with stirring. The oil bath was raised and the reaction mixture heated with stirring for an additional 20 minutes after the n-butanol addition. The reaction mixture was cooled and filtered. The excess solvent and n-butanol were stripped from the filtrate at room temperature under high vacuum. Very little residue remained. HPLC analysis of this residue did not detect the presence of trisbutylcarbamoyltriazine.

COMPARATIVE EXAMPLE 2

[0051] A 25 ml 3-neck round bottom flask was fitted with a dry ice condenser and a magnetic stirrer. The flask was also connected to a nitrogen source and a nitrogen atmosphere was maintained at ambient pressure. The flask was charged with melamine (1 gram). Phosgene (10 ml) was then condensed into the flask. The resulting slurry was stirred for 7 hours at a reflux temperature of phosgene. The phosgene was then vented to a scrubber. N-Butanol was then added to the reaction mixture. Analysis of the residue showed no trisbutylcarbamoyl-1,3,5-triazine.

COMPARATIVE EXAMPLE 3

[0052] Melamine (1.5 grams) and nitrobenzene (20 ml) were mixed in a 110 ml Hastelloy c-276 can. The can was sealed and placed inside a FIKE Vent Sizing Package. The can was cooled with dry ice and evacuated. Phosgene (20 grams) was condensed into the can. The dry ice was allowed to evaporate and the can heated to 100°C for 3 hours and 20 minutes. The pressure in the reaction vessel rose to 102 psig (8.0×10^5 Pa). Thereafter, the heat was turned off and the vessel vented. n-Butanol (10 ml) was injected into the reactor. HPLC analysis of the reaction mixture revealed no detectable trisbutylcarbamoyl-1,3,5-triazine.

[0053] Other variations and modifications of this invention will be obvious to those skilled in this art. This invention is not limited except as set forth in the following claims.

Claims

1. A process for preparing at least trisisocyanate functional derivatives by contacting (i) an amino-1,3,5-triazine and (ii) phosgene in a reaction system, at a temperature of 51.4°C to 120°C, a pressure of 50 psig (3.45 * 10^5 Pa) to 1000 psig (6.9 * 10^6 Pa) and for a length of time sufficient to produce an isocyanate functional 1,3,5-triazine derivative and hydrogen chloride, whereby the amino-1,3,5-triazine is an (at least tris-unsubstituted amino)-1,3,5-triazine, the reaction is conducted under conditions whereby the hydrogen chloride is gaseous and the phosgene is refluxed and at least a portion of the hydrogen chloride is removed from the reaction system as such hydrogen chloride is generated during the reaction of (i) and (ii) by passing an inert gas through the pressurized and heated reaction system during the reaction.

2. The process of claim 1, **characterized in that** the (at least tris-unsubstituted amino)-1,3,5-triazine comprises melamine or an oligomer thereof.

3. The process of claim 1 or 2, **characterized in that** the inert gas is argon or nitrogen.

4. The process of one of the preceding claims, **characterized in that** the relative amounts of the (at least tris-unsubstituted amino)-1,3,5-triazine and phosgene employed in the process is in the range of about 1:3 to about 1:250 on a weight basis.

5. A process for preparing at least trisisocyanate-based derivatives of (at least tris-unsubstituted amino)-1,3,5-triazines comprising the steps of:

   (a) preparing an isocyanate functional derivative of an amino-1,3,5-triazine as set forth in any one of claims 1 to 4; and
   (b) reacting an isocyanate-reactive material with the so-prepared isocyanate functional derivative.

6. The process according to claim 5, **characterized in that** the isocyanate-reactive material is an active-hydrogen containing compound selected from the group consisting of alcohols, phenols, oximes, hydroxamic acid ethers, lactams and mixtures thereof.

7. The process according to claim 6, **characterized in that** the active-hydrogen containing compound comprises an alcohol selected from the group consisting of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, tert-butanol, pentanol, hexanol, cyclo-hexanol, heptanol, octanol, ethylhexyl alcohol, benzyl alcohol, allyl alcohol, ethylene chlorhydrin, ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, ethoxyethanol, hydroxyethoxyethanol, 1-methoxy-2-propanol and mixtures thereof.

8. The process according to one of claims 5-7, **characterized in that** the isocyanate-reactive material is an isocyanate blocking agent.

Patentansprüche

1. Verfahren zur Herstellung von mindestens tris-isocyanat-funktionalen Derivaten, indem (i) ein Amino-1,3,5-triazin und (ii) Phosgen in einem Reaktionssystem bei einer Temperatur von 51,4 °C bis 120 °C, einem Druck von 50 psig (3,45 * 10^5 Pa) bis 1000 psig (6,9 * 10^6 Pa) und für eine Zeitdauer kontaktiert werden, die ausreichen, um ein isocyanat-funktionales 1,3,5-Triazinderivat und Chlorwasserstoff zu produzieren, wobei das Amino-1,3,5-triazin ein (mindestens tris-unsubstituiertes Amino)-1,3,5-triazin ist, die Reaktion unter Bedingungen durchgeführt wird, bei denen der Chlorwasserstoff gasförmig ist und das Phosgen unter Rückfluss gehalten wird und mindestens ein Teil des Chlorwasserstoffs aus dem Reaktionssystem entfernt wird, wenn dieser Chlorwasserstoff während der Reaktion von (i) und (ii) erzeugt wird, indem während der Umsetzung ein Inertgas durch das unter Druck stehende und erwärmte Reaktionssystem geleitet wird.

2. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das (mindestens tris-unsubstituierte Amino)-1,3,5-triazin Melamin oder ein Oligomer davon umfasst.

3. Verfahren gemäß Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** das Inertgas Argon oder Stickstoff ist.

4. Verfahren gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die relativen Mengen des (mindestens tris-unsubstituierten Amino)-1,3,5-triazins und Phosgens, die in dem Verfahren verwendet werden, im Bereich von etwa 1:3 bis etwa 1:250 auf Gewichtsbasis liegen.

5. Verfahren zum Herstellen von mindestens Tris-isocyanat-basierten Derivaten von (mindestens tris-unsubstituierten Amino)-1,3,5-triazinen, umfassend die Schritte:

   (a) Herstellen eines isocyanat-funktionalen Derivats von Amino-1,3,5-triazin, wie in einem der Ansprüche 1 bis 4 beschrieben; und

   (b) Umsetzen von isocyanat-reaktivem Material mit dem so hergestellten isocyanat-funktionalen Derivat.

6. Verfahren gemäß Anspruch 5, **dadurch gekennzeichnet, dass** das isocyanat-reaktive Material eine aktiven Wasserstoff enthaltende Verbindung ausgewählt aus der Gruppe bestehend aus Alkoholen, Phenolen, Oximen, Hydroxamsäureethern, Lactamen und Mischungen derselben ist.

7. Verfahren gemäß Anspruch 6, **dadurch gekennzeichnet, dass** die aktiven Wasserstoff enthaltende Verbindung einen Alkohol ausgewählt aus der Gruppe bestehend aus Methanol, Ethanol, 1-Propanol, 2-Propanol, 1-Butanol, 2-Butanol, Isobutanol, tert.-Butanol, Pentanol, Hexanol, Cyclohexanol, Heptanol, Octanol, Ethylhexylalkohol, Benzylalkohol, Allylalkohol, Ethylenchlorhydrin, Ethylenglykol, Propylenglykol, 1,3-Propandiol, 1,4-Butandiol, Ethoxyethanol, Hydroxyethoxyethanol, 1-Methoxy-2-propanol und Mischungen derselben umfasst.

8. Verfahren gemäß einem der Ansprüche 5 bis 7, **dadurch gekennzeichnet, dass** das isocyanat-reaktive Material ein Isocyanat-Blockierungsmittel ist.

Revendications

1. Procédé de préparation de dérivés à fonction au moins tri-isocyanate comprenant l'étape consistant à mettre en contact (i) une amino-1,3,5-triazine et (ii) un phosgène dans un système réactionnel, à une température de 51,4 à 120°C, une pression de 50 psig (3,45 x 10^5 Pa) à 1000 psig (6,9 x 10^6 Pa) et pendant une durée de temps suffisante pour produire un dérivé de 1,3,5-triazine à fonction isocyanate et du chlorure d'hydrogène, dans lequel l'amino-1,3,5-triazine est une (au moins trisamino non substitué)-1,3,5-triazine, la réaction est mise en oeuvre dans des conditions telles que le chlorure d'hydrogène soit gazeux et que le phosgène soit sous reflux, et au moins une partie du chlorure d'hydrogène soit éliminée du système réactionnel au fur et à mesure que le chlorure d'hydrogène est généré pendant la réaction de (i) et (ii) en faisant passer un gaz inerte dans le système réactionnel sous pression et chauffé pendant la réaction.

2. Procédé selon la revendication 1, **caractérisé en ce que** la (au moins trisamino non substitué)-1,3,5-triazine comprend la mélamine ou un de ses oligomères.

3. Procédé selon la revendication I ou 2, **caractérisé en ce que** le gaz inerte est l'argon ou l'azote.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** les quantités relatives de la (au moins trisamino non substitué)-1,3,5-triazine et du phosgène utilisés dans le procédé sont dans la plage d'environ 1:3 à environ 1:250 sur une base en poids.

5. Procédé de préparation de dérivés au moins à base de tri-isocyanate de (au moins trisamino non substitué)-1,3,5-triazines comprenant les étapes consistant à :

   (a) préparer un dérivé à fonction isocyanate d'une amino-1,3,5-triazine comme exposé dans l'une quelconque des revendications 1 à 4 ; et
   (b) faire réagir un matériau réagissant avec les isocyanates avec le dérivé à fonction isocyanate ainsi préparé.

6. Procédé selon la revendication 5, **caractérisé en ce que** le matériau réagissant avec les isocyanates est un composé contenant de l'hydrogène actif choisi dans le groupe composé des alcools, des phénols, des oximes, des éthers d'acide hydroxamique, des lactames et de leurs mélanges.

7. Procédé selon la revendication 6, **caractérisé en ce que** le composé contenant de l'hydrogène actif comprend un alcool choisi dans le groupe composé du méthanol, de l'éthanol, du 1-propanol, 2-propanol, 1-butanol, 2-butanol, de l'isobutanol, du tert-butanol, du pentanol, de l'hexanol, du cyclohexanol, de l'heptanol, de l'octanol, de l'alcool éthylhexylique, de l'alcool benzylique, de l'alcool allylique, de l'éthylène chlorhydrine, de l'éthylène glycol, du propylène glycol, du 1,3-propanediol, 1,4-butanediol, de l'éthoxyéthanol, de l'hydroxyéthoxyéthanol, du 1-méthoxy-2-propanol et de leurs mélanges.

8. Procédé selon l'une quelconque des revendications 5 à 7, **caractérisé en ce que** le matériau réagissant avec les isocyanates est un agent de blocage d'